Abstract

Hydrogen economy is a cutting edge technology which utilises the fuel cell to obtain the electrical energy by means of chemical reaction between hydrogen and oxygen. Fuel cells provide a very efficient and clean source of electrical energy. However, the need of efficient storage system is a key problem of hydrogen economy. Hydrogen storage on solid materials via adsorption is an ingenious alternative.

There are various solid-state H₂ storage materials, which are presently being investigated. However, no material is found to have all the properties required for practical storage of hydrogen. Due to the growing need of energy, it is essential to use currently existing technologies along with development of new H₂ storage materials. Experimentally, this is a time taking process. Furthermore, it requires significant individual and economic resources. Computational materials science, in comparison, is a fast and efficient way for designing novel materials. Moreover, theoretical results can also validate experimental results. Consequently, the primary motivation of this thesis is to apply computational material science to design new different classes of H₂ storage materials and to explore the fundamental interactions involved in these materials.

The motivation of this thesis is to use a computational approach to investigate different hydrogen storage materials. In the thesis we will be specifically studying Metal Organic Frameworks (MOF) based materials due to their tremendous promise for the purpose of hydrogen storage and the need for enhancing their hydrogen storage properties. To this end, in this thesis we have performed density functional theory (DFT) based calculations to study theoretically the ground state lattice structure, electronic structure; effect of dopants, new MOF and ZIF based materials via novel dopants, of these hydrogen storage materials. The effect of boron substitution followed by metals decoration has also been studied using detailed molecular orbital analysis.
Thesis organization:

**Chapter 1 Introduction**

In this chapter, we will give a brief introduction to fuel cells and their advantages and applications. This will be followed by explanation of the use of hydrogen as a fuel for fuel cells. Thereafter, we will provide a brief discussion on the problems associated with hydrogen storage. We will explain the various mechanisms of solid-state hydrogen storage. Furthermore, we will review few hydrogen storage materials, namely, ammonia borane, clathrate hydrates, metal organic frameworks, and complex metal hydrides. We will end the chapter by describing the motivation behind the research carried out and by presenting an outline of the thesis.

**Chapter 2 Theoretical background**

In this chapter we will present a brief introduction to the theory behind the methodology used in the thesis. Firstly, we will give a brief introduction to the many-body problem by using Hartree approximation, the Hartree-Fock (HF) approximation, and the methods which go beyond HF. Thereafter, we will provide a discussion on the use of density functional theory (DFT). This will be followed by a description of the concepts of molecular dynamics and *ab initio* molecular dynamics. At the end, we will discuss the implementation of the plane wave-pseudopotential molecular dynamics method in the program package of VASP.

**Chapter 3 Electronic structure**

In this chapter we will begin MO treatment of band theory. Later we will discuss the different tools available for studying electronic structure of solids. Our results of the charge density, band structure, and density of states (DOS) analyses on pure and Mn-doped and pure ZNO will be presented. We will illustrate from the band structure and DOS calculations that Mn doping reduces the band gaps of the three phases of Zno. By examination of the partial DOS, it will be further shown that this reduction in band gaps is due to generation of additional bands arising from the Mn impurities. Finally, the decreased
band gaps will be used to suggest that doping with Mn in ZnO makes this material suitable to be used for photoelectrochemical splitting of water to produce hydrogen.

Chapter 4 Light Metal decorated MOF
In Chapter 4, the effect of light metal (M = Li, Be, Mg, and Al) decoration on the stability of metal organic framework MOF-5 and its hydrogen adsorption is investigated by ab initio and periodic density functional theory (DFT) calculations by employing models of the form BDC:M2:nH2 and MOF-5:M2:nH2, where BDC stands for the benzenedicarboxylate organic linker and MOF-5 represents the primitive unit cell. The suitability of the periodic DFT method employing the GGAPBE functional is tested against MP2/6-311+G* and MP2/cc-pVTZ molecular calculations. A correlation between the charge transfer and interaction energies is revealed. The metal-MOF-5 interactions are analyzed using the frontier molecular orbital approach. Difference charge density plots show that H2 molecules get polarized due to the charge generated on the metal atom adsorbed over the BDC linker, resulting in electrostatic guest-host interactions. Our solid state results show that amongst the four metal atoms, Mg and Be decoration does not stabilize the MOF-5 to any significant extent. Li and Al decoration strengthened the H2-MOF-5 interactions relative to the pure MOF-5 exhibited by the enhanced binding energies. The hydrogen binding energies for the Li- and Al-decorated MOF-5 were found to be sensible for allowing reversible hydrogen storage at ambient temperatures. A high hydrogen uptake of 4.3 wt.% and 3.9 wt.% is also predicted for the Li- and Al-decorated MOF-5, respectively.

Chapter 5 Transition metals novel dopants for MOF
Transition-metal-based systems show promising binding energy for hydrogen storage but suffer from clustering problem. The effect of light transition metal (M = Sc, Ti) decoration, boron substitution on the hydrogen storage properties of MOF-5, and clustering problem of metals has been investigated using ab initio density functional theory. Our results of solid-state calculations reveal that whereas Ti clusters strongly Sc atoms do not suffer from this problem when decorating MOF-5. Boron substitution on
metal-decorated MOF-5 enhances the interaction energy of both the metals with MOF-5. Sc-decorated MOF-5 shows a hydrogen storage capacity of 5.81 wt % with calculated binding energies of 20−40 kJ/mol, which ensures the room-temperature applicability of this hydrogen storage material. Furthermore, we have studied ZIF-72 a hydrogen storage material by studying hydrogen adsorption sites and metal decoration.

Chapter 6 Why Boron Substitution Increases the Interaction Energies of Metals with Benzene Based MOFs
To tune the interaction energies of metals with host materials and their H\textsubscript{2} binding energies (E\textsubscript{binding}), boron substitution in the framework has been widely pursued. The investigation of role of boron substitution in enhancement of the interaction energies is necessary for designing new and potential storage materials. Our results demonstrate that boron substitution provides the proper symmetry in the framework to overlap with the metals orbitals. These orbital interactions increase the host-guest interactions, leading to increase in the interaction energies. We have also investigated the nature of interaction of H\textsubscript{2} molecules with metals in metal decorated-boronsubstituted benzene as a model system for benzene based MOFs